Synthesis and Reactions of Alkyl Fluorocarbamates and Difluorocarbamates[1]

Vytautas Grakauskas and Kurt Baum

Contribution of the Environmental Systems Division, Aerojet-General Corporation, Azusa, California. *Received November 12, 1968*

Abstract: Alkyl fluorocarbamates and alkyl difluorocarbamates were synthesized by the direct fluorination of alkyl carbamates in aqueous and nonaqueous solutions, respectively. Ethyl fluorocarbamate formed salts with aqueous alkali which reacted with dimethyl sulfate, ethyl chloroformate, chlorine, and bromine to give, respectively, ethyl N-fluoro-N-methylcarbamate, diethyl N-fluoroiminodicarboxylate, ethyl chlorofluorocarbamate, and ethyl bromofluorocarbamate. Dichlorofluoramine was prepared from ethyl fluorocarbamate and excess sodium hypochlorite. Ethyl fluorocarbamate reacted with aldehydes in the presence of a trace of acid to give carbethoxyfluoraminocarbinols, and, at higher temperatures, bis(carbethoxyfluoramino)alkanes. Ethyl vinyl ether gave ethyl N-α-ethoxyethyl-N-fluorocarbamate. Ethyl fluorocarbamate in concentrated sulfuric acid reacted with cyclohexene, cyclopentene, and methyl acrylate to give ethyl N-cyclohexyl-N-fluorocarbamate, ethyl N-cyclopentyl-N-fluorocarbamate, and methyl N-carbethoxy-N-fluoro-β-aminopropionate, respectively. Alkyl difluorocarbamates reacted with water, alcohols, and sodium hypochlorite to give difluoramine, dialkyl carbonates, and chlorodifluoramine, respectively.

The first reported example of the fluorination of a nitrogenous compound in aqueous solution was the synthesis of N,N-difluorourea from urea.[2] Subsequently, the fluorination of carbamates was studied in these laboratories using both aqueous and nonaqueous solutions. Recently, Banks, Haszeldine, and Lalu[3] have reported that the fluorination of aqueous urethan with 2 mol of fluorine gave a 30% yield of ethyl fluorocarbamate. The present paper describes the synthesis of both alkyl fluorocarbamates and alkyl difluorocarbamates by the direct fluorination of carbamates and the chemical properties of the products.

Alkyl fluorocarbamates were synthesized in about 30% conversion by the reaction of aqueous solutions of carbamates with 1 mol of fluorine. Further fluorination reduced the amount of unreacted starting material, but did not increase appreciably the conversion to fluorocarbamates. Difluoramine, however, could be condensed from the exhaust gases. It appeared therefore that the alkyl fluorocarbamates were fluorinated at a rate comparable to that of the fluorination of carbamates and that the resulting difluorocarbamates underwent relatively rapid hydrolysis.

$$ROCNH_2 \xrightarrow[H_2O]{F_2} ROCNHF \xrightarrow{F_2}$$

$$\left[ROCNF_2\right] \xrightarrow{H_2O} ROH + CO_2 + HNF_2$$

R = CH_3, C_2H_5, $CH(CH_3)_2$, $CH_2CH_2CH_2CH_3$

Consequently, the corresponding alkyl difluorocarbamates were isolated by using nonaqueous solvents for the fluorinations, such as carbon tetrachloride, methylene chloride, 1,1,2-trichloro-1,2,2-trifluoroethane, and acetonitrile. Acetonitrile is preferred because of its low reactivity with fluorine and high solvent power for the starting materials.[4] Yields of alkyl difluorocarbamates of over 90% were indicated by gas chromatographic analysis of the fluorination mixtures obtained by passing 2 mol of fluorine into acetonitrile solutions of carbamates. The bulk of the solvent could be removed by washing with ice water, and the pure difluorocarbamates were obtained by distillation (or gas chromatography where the boiling points were close to that of the solvent), with yields to 76%.

$$ROCNH_2 \xrightarrow[CH_3CN]{F_2} ROCNF_2$$

R = CH_3, C_2H_5, $CH(CH_3)_2$, $CH_2CH_2CH_2CH_3$

Methyl chlorocarbamate has been reported to be sufficiently acidic to form alkali salts in aqueous solution.[5] Alkyl fluorocarbamates were found likewise to be soluble in cold aqueous alkali, and could not be extracted from the alkaline solutions with organic solvents. Acidification, however, resulted in recovery of the starting materials. The alkyl fluorocarbamate salts decomposed rapidly in solution at room temperature, but were sufficiently stable at 0–5° for the preparation of derivatives. This relatively high stability compared to that of difluoramine in the presence of base[6] is attributed to resonance stabilization of the negative charge by the carbonyl group.

$$ROCNHF \xrightarrow[0°]{NaOH} ROCNF^- \longleftrightarrow ROC{=}NF$$

(1) Supported by the Office of Naval Research and the Advanced Research Projects Agency. Presented in part at the Third International Fluorine Symposium, Munich, Sept 1965.

(2) V. Grakauskas, Abstracts of the 140th National Meeting of the American Chemical Society, Sept 1961, p 23M.

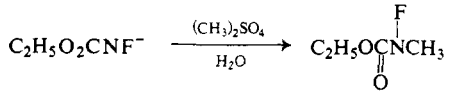
(3) R. E. Banks, R. N. Haszeldine, and J. P. Lalu, *J. Chem. Soc., C*, 1514 (1966).

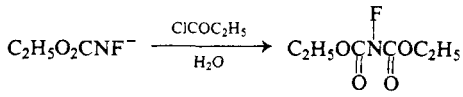
(4) The fluorination of suspensions of the substrate frequently results in localized ignition at the fluorine inlet.

(5) P. Chabrier, *Ann. Chim.*, [11] **17**, 353 (1942).

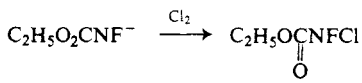
(6) K. J. Martin, *J. Am. Chem. Soc.*, **87**, 394 (1965); A. D. Craig and G. A. Ward, *ibid.*, **88**, 4526 (1966); W. T. Yap, A. D. Craig, and G. A. Ward, *ibid.*, **89**, 3442 (1967).

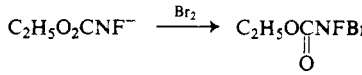
The sodium salt of ethyl fluorocarbamate in aqueous solution was found to react with a variety of electrophilic reagents. Thus, dimethyl sulfate gave ethyl N-fluoro-N-methylcarbamate and ethyl chloroformate gave diethyl N-fluoriminodicarboxylate.

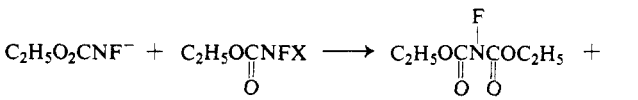




Halogenation of aqueous solutions of the salt of ethyl fluorocarbamate with the theoretical amounts of chlorine and bromine gave ethyl chlorofluorocarbamate and ethyl bromofluorocarbamate, respectively. A by-product of these halogenations was diethyl N-fluoriminodicarboxylate, which was most likely formed by the acylation of the salt of ethyl fluorocarbamate by the halofluorocarbamate. This reaction is analogous to the function of difluorocarbamates as acylating agents, described below.



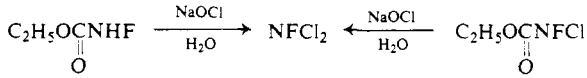




[NFX$^-$]

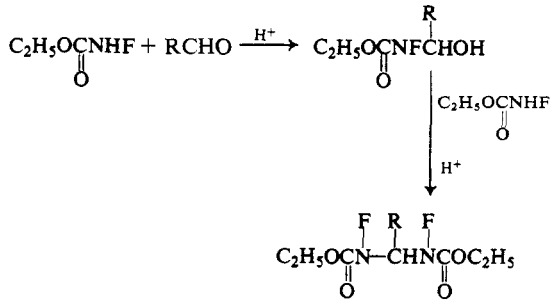
Compounds having bromine and fluorine on a nitrogen atom have not been reported previously. Only two organic N-chloro-N-fluoramino compounds have been reported, N-fluoro-N-chlorotrifluoromethylamine[7] and N-chloro-N-fluoro-1,1-difluoroethylamine.[8]

The reaction of ethyl fluorocarbamate or ethyl chlorofluorocarbamate with an excess of aqueous sodium hypochlorite gave dichlorofluoramine. Dichlorofluoramine was prepared previously by the reaction of chlorine monofluoride with sodium azide.[9]



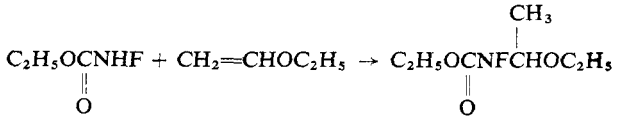
The NH of ethyl fluorocarbamate was also found to be labile under acidic conditions. It was of interest to compare reactions of aldehydes with fluorocarbamates, carbamates, and difluoramine. Alkyl carbamates have been reported to give alkylidenedicarbamates in the presence of a catalytic amount of acid, but attempts to isolate 1:1 condensation products were unsuccessful.[10] Difluoramine, on the other hand, gave α-difluoraminocarbinols in a readily reversible reaction on mixing the reagents,[11] and 1,1-bis(difluoramino)alkanes in highly acidic media.[12]

Ethyl fluorocarbamate was found to react with aqueous formaldehyde in the presence of a trace of acid to give ethyl N-fluoro-N-(hydroxymethyl)carbamate. Similarly, the reaction of ethyl fluorocarbamate with undiluted butyraldehyde gave ethyl N-fluoro-N-α-hydroxybutylcarbamate. The latter reaction also proceeded readily in the reverse direction, and spectra of the distilled product showed the presence of the starting materials as well as adduct. The carbinols reacted further with ethyl fluorocarbamate at 60° in the presence of a trace of acid to give diethyl N,N′-difluoromethylenedicarbamate and 1,1-bis(carbethoxyfluoramino)butane, respectively.



The fact that a monoadduct of a simple carbamate and an aldehyde cannot be isolated indicates that the carbinol is converted rapidly to a carbonium ion stabilized by nitrogen. The electron-withdrawing fluorine of the fluorocarbamate reduces this stabilization sufficiently to make the carbinol less reactive than the original aldehyde.

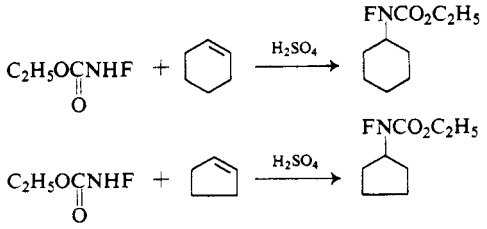
Ethyl fluorocarbamate was also added to ethyl vinyl ether in the presence of a trace of hydrochloric acid to give ethyl N-α-ethoxyethyl-N-fluorocarbamate.



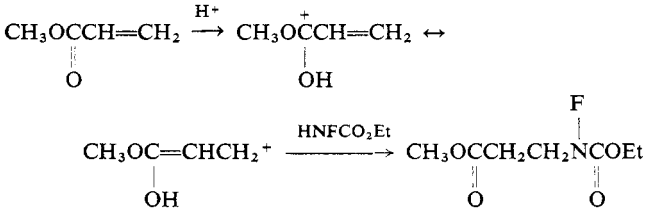
Some reactions of ethyl fluorocarbamate in concentrated sulfuric acid were studied. Difluoramine has been alkylated by olefins such as isobutylene in this solvent,[13] but the products rearranged rapidly to fluorimonium ions.[14,15] The isolation of the difluoramine adduct of cyclohexene required the use of a milder catalyst such as the boron trifluoride complex of phosphoric acid,[13,15] but the adduct of cyclopentene could not be isolated under these conditions. By contrast, ethyl fluorocarbamate and cyclohexene in sulfuric acid gave an 82% yield of ethyl N-cyclohexyl-N-fluorocarbamate after 45 min at room temperature. Cyclopentene under the same conditions gave a 34% yield of ethyl N-cyclopentyl-N-fluorocarbamate.

Methyl acrylate reacted with ethyl fluorocarbamate in sulfuric acid to give methyl N-carbethoxy-N-fluoro-β-aminopropionate, the product of alkylation by the ter-

(7) J. B. Hynes, B. C. Bishop, and L. A. Bigelow, *Inorg. Chem.*, **6**, 417 (1967).
(8) M. Lustig, *ibid.*, **6**, 1064 (1967).
(9) B. Sukornick, R. F. Stahl, and J. Gordon, *ibid.*, **2**, 875 (1963).
(10) W. M. Kraft and R. M. Herbst, *J. Org. Chem.*, **10**, 483 (1945).
(11) J. P. Freeman, W. H. Graham, and C. O. Parker, *J. Am. Chem. Soc.*, **90**, 121 (1968).
(12) K. Baum, *ibid.*, **90**, 7083 (1968).
(13) W. H. Graham and J. P. Freeman, *ibid.*, **89**, 716 (1967).
(14) K. Baum and H. M. Nelson, *ibid.*, **88**, 4459 (1966).
(15) K. Baum, *J. Org. Chem.*, **32**, 3648 (1967).



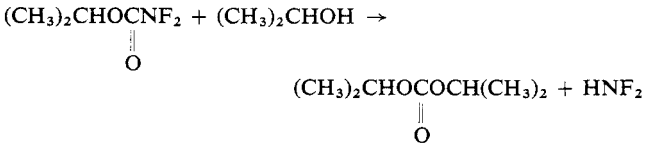
minal position of the resonance-stabilized protonated ester. This Michael addition is similar to the corresponding reaction of difluoramine.[12]



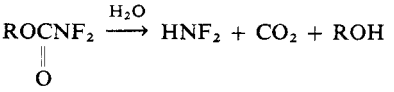
Reactions of alkyl fluorocarbamates with strong acids to give the fluorammonium ion have been reported previously,[16] and the above addition reactions were conducted at temperatures at which cleavage of the ester groups does not take place at an appreciable rate. The stability of the adducts in sulfuric acid may be attributed to protonation of the ester groups.

A more limited study was made of the chemical properties of alkyl difluorocarbamates. The compounds showed reactivity similar to that of alkyl haloformates, with the difluoramino group functioning as a pseudohalogen. This mode of reaction corresponds to that reported for N,N-difluoramides, which were prepared from tetrafluorohydrazine and acyl radicals.[17]

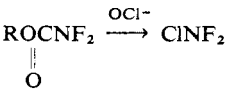
Thus, isopropyl difluorocarbamate reacted with isopropyl alcohol to give diisopropyl carbonate.



Butyl difluorocarbamate and isopropyl difluorocarbamate had low solubility in water and hydrolyzed relatively slowly at room temperature when the mixtures were not stirred. Hydrolysis was rapid in 25% sulfuric acid at 70° and an 89% yield of difluoramine was obtained from butyl difluorocarbamate.



Chlorodifluoramine was prepared by the reaction of butyl difluorocarbamate with aqueous sodium hypochlorite. The analogous reaction using N,N-difluorosulfamide has been reported.[18]



(16) V. Grakauskas, A. H. Remanick, and K. Baum, *J. Am. Chem. Soc.*, **90**, 3839 (1968).
(17) R. C. Petry and J. P. Freeman, *ibid.*, **83**, 3912 (1961).
(18) R. A. Wiesboeck and J. K. Ruff, *Inorg. Chem.*, **4**, 123 (1965).

Experimental Section

General. Fluorinations were conducted in a glass standard taper three-necked flask fitted with a mechanical stirrer, a glass tube extending below the liquid level used as a gas inlet, and a standard taper thermometer well with an opening for gas exit. Standard fluorine-handling hardware[19] was used, and the fluorine was diluted with nitrogen. Exit gases were vented through an aqueous potassium iodide trap. Safety shielding is required for the fluorinations and for handling NF compounds.

Methyl Fluorocarbamate. A solution of 75 g (1.00 mol) of methyl carbamate in 500 ml of water was fluorinated at 0–5°, with stirring, until 1 mol of fluorine (diluted fourfold with nitrogen) was absorbed. The product was extracted with ten 50-ml portions of ether, and the ether solution was dried and distilled through a concentric tube column to give 25 g (27% yield) of methyl fluorocarbamate, bp 62–63° (26 mm), $n^{25}D$ 1.3895.

Anal. Calcd for $C_2H_4NO_2F$: C, 25.81; H, 4.33; N, 15.05; F, 20.42. Found: C, 25.50; H, 4.41; N, 15.0; F, 20.4.

The infrared spectrum showed the following peaks (μ): 3.01 (m), 3.28 (w), 3.38 (w), 5.64 (s), 5.75 (s), 6.95 (s), 7.13 (m), 7.49 (s), 7.9 (sh), 8.10 (s), 8.39 (m), 9.30 (s), 9.50 (s), 9.75 (m), 9.90 (m), 10.60 (w), 11.40 (w), and 17.40 (m). The proton nmr spectrum (chloroform solution) consisted of a singlet at δ 4.02 for the methyl and a doublet (J = 57 cps) at δ 10.10 for the NH. The fluorine spectrum consisted of a doublet (J = 56 cps) at ϕ^* +119.1.

Difluoramine was detected in the exit gases. It was condensed with a −80° trap and identified by its infrared spectrum.[20]

Ethyl Fluorocarbamate. The above procedure gave a 27% yield of ethyl fluorocarbamate, with physical and spectral properties identical with reported values.[3] A 60-cm Stedmann column was used for the distillation.

Isopropyl Fluorocarbamate. The above procedure gave a 33% yield of isopropyl fluorocarbamate, bp 29–30° (0.1 mm), $n^{25}D$ 1.3970.

Anal. Calcd for $C_4H_8NO_2F$: C, 39.67; H, 6.66; N, 11.57; F, 15.69. Found: C, 39.50; H, 6.41; N, 11.5; F, 15.4.

The infrared spectrum showed the following peaks (μ): 3.10 (s), 3.37 (m), 3.40 (m), 3.48 (w), 3.65–3.85 (s), 6.9 (s), 7.25 (s), 7.6 (m), 7.95 (s), 8.47 (m), 8.73 (m), 9.07 (s), 9.4 (s), 9.75 (s), 10.65 (w), 11.0 (m), 11.95 (s), 12.3 (sh), 13.2 (m), and 14.0 (w). The proton nmr spectrum (deuteriochloroform solution) consisted of a doublet (J = 6.3 cps) at δ 1.33 for the methyls, a septet (J = 6.3 cps) at δ 5.07 for the methine, and a doublet (J = 55.9) at δ 9.60 for the NH. The fluorine spectrum showed a doublet (J = 55.5) at ϕ^* +115.70.

Butyl Fluorocarbamate. The above procedure gave a 24% yield of butyl fluorocarbamate, bp 36–37° (0.1 mm).

Anal. Calcd for $C_5H_{10}NO_2F$: C, 44.44; H, 7.46; N, 10.37; F, 14.06. Found: C, 44.81; H, 7.39; N, 10.1; F, 14.0.

The infrared spectrum showed the following peaks (μ): 3.15 (m), 3.21 (m), 3.52 (m), 5.70 (s), 6.9 (s), 7.45 (m), 7.95 (s), 9.3 (s), 9.65 (s), 10.4 (w), 10.7 (w), 11.9–12.5 (m), and 13.4–13.7 (m). The proton nmr spectrum ($DCCl_3$ solution) showed a triplet at δ 4.26 for the α-methylene, a multiplet with maximum intensity at 1.6 for the other methylenes, a triplet at 0.94 for the methyl, and a doublet (J = 55.5) at 9.42 for NH. The fluorine spectrum consisted of a doublet (J = 56.1) at ϕ^* +114.88.

Ethyl Difluorocarbamate. A solution of 89 g (1.0 mol) of ethyl carbamate in 230 ml of acetonitrile was fluorinated at −20 to −30° until 2.0 mol of fluorine was consumed (3.5 hr). Analysis by gas chromatography (3 ft × $^3/_{16}$ in. column of diethylene glycol adipate, 50°, 50 cc/sec of helium) indicated a 92% yield of ethyl difluorocarbamate. A 10% aliquot of this acetonitrile solution was washed with four 100-ml portions of ice water to give 4.8 g of a 9:1 mixture of ethyl difluorocarbamate and acetonitrile (gc retention times, 8 and 2.4 min, respectively, at the above conditions) containing a trace of fluoroacetonitrile. The material, bp 31–35° (100 mm), could not be purified readily by distillation; an analytical sample was isolated by gas chromatography.

Anal. Calcd for $C_3H_5NF_2O_2$: C, 28.81; H, 4.03; N, 11.20. Found: C, 29.19; H, 4.40; N, 11.0.

The proton nmr spectrum showed a triplet at δ 1.25 and a quartet at 4.16 (J = 7.2 cps). The fluorine spectrum showed a broadened band at ϕ^* −33.0. The infrared spectrum showed strong bands 5.50 and 8.0 μ. Higher fluorine to substrate ratios,

(19) Allied Chemical Corp., Data Sheet PD-TA-85413A.
(20) C. B. Colburn, *Advan. Fluorine Chem.*, **3**, 113 (1963).

which would be expected to yield NF_3 or alkyl fluorination products, were not examined.

Methyl Difluorocarbamate. The above procedure was used, and the proximity of the boiling point of the product, 37–38° (150 mm), to that of the solvent again required gc purification. The proton nmr spectrum consisted of a singlet at δ 4.10.

Anal. Calcd for $C_2H_3NF_2O_2$: C, 21.63; H, 2.72; N, 12.61. Found: C, 22.00; H, 2.91; N, 12.2.

Isopropyl Difluorocarbamate. A solution of 103 g (1.0 mol) of isopropyl carbamate in 550 ml of acetonitrile was fluorinated at −10 to −15° until 2.0 mol of fluorine was consumed (4.0 hr). The solution was added to 3 l. of ice water. The organic phase was separated and washed with one 2200-ml portion and with three 600-ml portions of ice water. The product was dried over sodium sulfate and distilled to give 106 g (76% yield) of colorless liquid, bp 28° (40 mm).

Anal. Calcd for $C_4H_7NF_2O_2$: C, 34.54; H, 5.08; N, 10.07; F, 27.32. Found: C, 34.81; H, 4.70; N, 9.9; F, 26.5.

The proton nmr spectrum consisted of a septet at δ 5.19 (CH) and a doublet at δ 1.44 (CH_3). The fluorine spectrum consisted of a singlet at ϕ^* −32.74. The infrared spectrum showed the following bands (μ): 3.34 (m), 5.51 (s), 5.78 (w), 6.80 (m), 7.17 (m), 7.23 (m), 7.4 (w), 7.9 (s), 8.41 (m), 8.69 (m), 9.09 (s), 9.68 (s), 10.67 (s), 11.55 (s), and 12.17 (s).

Butyl Difluorocarbamate. A solution of 93 g (0.8 mol) of butyl carbamate in 400 ml of acetonitrile was fluorinated at 0–5° until 2 mol of fluorine was absorbed (1.5 hr). The reaction mixture was washed as above and distilled to give 67.5 g (44% yield) of butyl difluorocarbamate, bp 65° (60 mm), $n^{25}D$ 1.3665.

Anal. Calcd for $C_5H_9NF_2O_2$: C, 39.21; H, 5.92; N, 9.15; F, 24.8. Found: C, 39.22; H, 6.21; N, 9.1; F, 25.1.

The distillation residue, 45 g, was an equal mixture of butyl carbamate and *n*-butyl N-fluorocarbamate, as determined by elemental analysis. The proton nmr spectrum showed an irregular triplet at δ 0.98 for the methyl, a triplet at 4.42 for $C(=O)OCH_2-$, and a multiplet with maximum intensity at 1.6 for the other methylenes. The fluorine spectrum showed a singlet at ϕ^* −32.8.

Sodium Salt of Ethyl Fluorocarbamate. Ethyl fluorocarbamate, 3.21 g (0.03 mol), was added dropwise, with stirring, at 0–3° to a solution of 1.2 g (0.03 mol) of sodium hydroxide in 20 ml of water. A pale-yellow solution resulted, from which fluorocarbamate could not be extracted with diethyl ether or methylene chloride at 0°. The solution was acidified with 20% sulfuric acid and was extracted with seven 15-ml portions of diethyl ether. Distillation of the dried ether solution gave 2.3 g (72% recovery) of ethyl fluorocarbamate.

Ethyl N-Fluoro-N-methylcarbamate. Dimethyl sulfate (5.05 g, 0.040 mol) was added dropwise, with stirring, to a solution of 8.6 g (0.08 mol) of ethyl fluorocarbamate in 80 ml of 1 *N* sodium hydroxide at 0–10°. This reaction temperature was maintained for 1 hr. The product was extracted with three 25-ml portions of methylene chloride, dried, and distilled to give 4.5 g (46% yield) of ethyl N-fluoro-N-methylcarbamate, bp 50° (25 mm), $n^{25}D$ 1.3870.

Anal. Calcd for $C_4H_8FNO_2$: C, 39.67; H, 6.66; N, 11.57; F, 15.69. Found: C, 39.32; H, 6.60; N, 11.97; F, 15.2.

The proton nmr spectrum consisted of a triplet at δ 1.31 and a quartet at 4.14 for the ethoxy group and a doublet (J_{HF} = 28 cps) at 3.29 for CH_3NF-. The fluorine spectrum consisted of a triplet (J = 28 cps) at ϕ^* +57.2. The infrared spectrum showed the following peaks (μ): 3.42 (m), 5.72 (s), 5.81 (s), 6.87 (m), 7.0 (m), 7.15 (m), 7.33 (m), 7.64 (s), 7.8 (sh), 8.49 (s), 8.6 (sh), 8.81 (m), 9.17 (m), 9.83 (m), 10.4 (w), 11.57 (w), 12.0 (m), 12.9 (m), and 13.6 (m).

Diethyl N-Fluoroiminodicarboxylate. Ethyl chloroformate (5.4 g, 0.050 mol) was added dropwise, with stirring, over a 10-min period to a solution of 5.4 g (0.050 mol) of ethyl fluorocarbamate in 50 ml of 1 *N* sodium hydroxide at 0 to 5°. An oil separated. The mixture was stirred for 10 min and was then extracted with two 25-ml portions of methylene chloride. The methylene chloride solution was dried and distilled to give 6.5 g (73% yield) of diethyl N-fluoroiminodicarboxylate, bp 55° (0.2 mm), $n^{25}D$ 1.4145.

Anal. Calcd for $C_6H_{10}FNO_4$: C, 40.22; H, 5.63; N, 7.82; F, 10.61. Found: C, 40.30; H, 5.81; N, 7.7; F. 10.9.

The infrared spectrum consisted of the following peaks (μ): 3.35 (m), 3.4 (sh), 5.60 (s), 6.79 (m), 6.87 (m), 7.15 (m), 7.8–8.4 (vs), 9.0 (s), 10.0 (s), 11.6 (m), and 13.4 (m). The proton nmr spectrum consisted of a triplet (J = 7.1 cps) at δ 1.38 for the methyls and a quartet (J = 7.1 cps) at 4.4 for the methylenes. The fluorine spectrum consisted of a singlet at ϕ^* 69.1.

Ethyl Chlorofluorocarbamate. Chlorine (0.04 mol) was passed into a stirred mixture of 25 ml of methylene chloride and a solution of 4.3 g (0.04 mol) of ethyl fluorocarbamate in 25 ml of 1.6 *N* sodium hydroxide at 0 to 5° over a 45-min period. The water-insoluble product was separated and the aqueous phase extracted with two 25-ml portions of methylene chloride. The organic phases were combined, dried over sodium sulfate, and distilled to give 3.2 g (57% yield) of ethyl chlorofluorocarbamate, bp 45° (60 mm), $n^{25}D$ 1.4015.

Anal. Calcd for $C_3H_5ClFNO_2$: C, 25.46; H, 3.56; N, 9.90; F, 13.42. Found: C, 25.80; H, 3.50; N, 9.8; F, 13.0.

The infrared spectrum showed peaks at (μ): 3.35 (w), 5.60 (s), 6.76 (w), 6.85 (w), 7.10 (w), 7.27 (m), 7.70 (m), 8.0 (s), 8.5 (w), 9.1 (w), 9.73 (s), 10.2 (w), 11.0 (s), 11.77 (m), 12.72 (m), and 13.3 (m). Further distillation of the residue gave 1.1 g of diethyl N-fluoroiminodicarboxylate, identical with an authentic sample.

Ethyl Bromofluorocarbamate. The above procedure, using 6.40 g (0.04 mol) of bromine instead of chlorine, gave 5.57 g (75% yield) of ethyl bromofluorocarbamate, bp 30° (0.1 mm), $n^{25}D$ 1.4421.

Anal. Calcd for $C_3H_5BrFNO_2$: C, 19.36; H, 2.71; N, 7.53; F, 10.20. Found: C, 19.80; H, 2.43; N, 7.60; F, 10.6.

The infrared spectrum was identical with that of ethyl chlorofluorocarbamate except that the last two peaks were shifted to 12.80 and 13.70. Diethyl N-fluoroiminodicarboxylate, 1.5 g, was obtained on distillation of the residue.

Dichlorofluoramine. Ethyl fluorocarbamate (5.4 g, 0.050 mol) was added dropwise, with stirring, to 150 ml of 5.4% aqueous sodium hypochlorite at 0 to 5° under a stream of nitrogen. A heavy liquid separated which was swept into a −80° trap connected to the reaction flask when the solution was warmed to room temperature. Trap-to-trap distillation gave 1.8 ml (at −20°) of dichlorofluoramine, with an infrared spectrum identical with that in the literature.[9] The reaction of 0.7 g of ethyl chlorofluorocarbamate with 20 ml of the hypochlorite solution similarly gave 0.3 ml of dichlorofluoramine.

Ethyl N-Fluoro-N-(hydroxymethyl)carbamate. Concentrated hydrochloric acid (0.1 ml) and 6.42 g (0.060 mol) of ethyl fluorocarbamate were added to 75 ml of aqueous 12% formaldehyde at 5°, and the mixture was allowed to stand at ambient temperature for 16 hr. The product was extracted with six 30-ml portions of methylene chloride, dried over Drierite, and distilled to give 6.4 g (78% yield) of ethyl N-fluoro-N-(hydroxymethyl)carbamate, bp 42–43° (0.2 mm), $n^{25}D$ 1.4180.

Anal. Calcd for $C_4H_8NFO_3$: C, 35.04; H, 5.85; N, 10.2; F, 13.9. Found: C, 34.99; H, 5.98; N, 10.35; F, 13.8.

The proton nmr spectrum (CCl_4 solution) consisted of a singlet for OH at δ 5.03, a doublet (J_{HF} = 33 cps) at 4.92 for $-NFCH_2-$, and a triplet at 1.37 and a quartet at 4.33 for the ethoxy group. The fluorine spectrum consisted of a triplet (J = 32 cps) at ϕ^* +74.9. The infrared spectrum of a thin film showed a broad OH band at 2.92 μ and a carbonyl band at 5.77 with a shoulder at 5.70; the spectrum of a CCl_4 solution showed a sharp OH band at 2.8, and carbonyl bands at 5.80 and 5.65.

Ethyl N-Fluoro-N-(α-hydroxybutyl)carbamate. One drop of concentrated hydrochloric acid was added to 5.5 g (0.076 mol) of butyraldehyde and 4.3 g (0.040 mol) of ethyl fluorocarbamate. External cooling was necessary for several minutes to keep the reaction temperature at 25–30°. The mixture was allowed to stand at room temperature for 16 hr. Distillation gave 5.5 g of ethyl N-fluoro-N-(α-hydroxybutyl)carbamate, bp 63–66° (0.2 mm).

Anal. Calcd for $C_7H_{14}FNO_3$: C, 46.92; H, 7.88; N, 7.82; F, 10.60. Found: C, 47.50; H, 8.46; N, 7.53; F, 10.80.

The nmr and ir spectra of the material showed that small amounts of both butyraldehyde and ethyl fluorocarbamate were present as impurities.

Diethyl N,N′-Difluoromethylenedicarbamate. A mixture of 6.85 g (0.050 mol) of ethyl N-fluoro-N-(hydroxymethyl)carbamate, 5.4 g (0.050 mol) of ethyl fluorocarbamate, and 0.05 ml of concentrated hydrochloric acid was heated at 60–65° for 16 hr. Distillation gave 4.5 g of ethyl fluorocarbamate, 3.4 g of ethyl N-fluoro-N-(hydroxymethyl)carbamate, and 2.3 g (20% conversion) of diethyl N,N′-difluoromethylenedicarbamate, bp 83–84° (0.2 mm), $n^{25}D$ 1.4232. The infrared spectrum showed carbonyl bands at 5.67 and 5.77 μ.

Anal. Calcd for $C_7H_{12}N_2F_2O_4$: C, 37.17; H, 5.35; N, 12.4; F, 16.8. Found: C, 36.80; H, 5.35; N, 12.3; F, 16.3.

1,1-Bis(carbethoxyfluoramino)butane. Hydrochloric acid (0.05 ml) was added to 10.7 g (0.10 mol) of ethyl fluorocarbamate and 3.6 g (0.050 mol) of butyraldehyde. Cooling was required for 5 min to keep the temperature below 50°. The mixture was then heated at 55–65° for 18 hr. Distillation gave 3.2 g of ethyl fluorocarbamate and 8.1 g (60% conversion, 86% yield) of 1,1-bis-

(carbethoxyfluoramino)butane, bp 81–82° (0.15 mm), $n^{25}D$ 1.4272.

Anal. Calcd for $C_{10}H_8N_2F_2O_4$: C, 44.77; H, 6.77; N, 10.44; F, 14.16. Found: C, 45.10; H, 6.53; N, 10.32; F, 14.4.

The proton nmr spectrum (CCl_4 solution) consisted of a triplet at δ 1.34 and a quartet at 4.33 for the ethoxy groups, a triplet at 1.0 for the other methyl, multiplets at 1.3 to 2.3 for the methylenes, and a triplet of triplets (J_{HF} = 35 cps, J_{HH} = 8.7 cps) at 5.94 for the methine. The infrared spectra showed a carbonyl band at 5.75 μ with a shoulder at 5.65.

Ethyl N-α-Ethoxyethyl-N-fluorocarbamate. One drop of concentrated hydrochloric acid was added to a mixture of 5.4 g (0.050 mol) of ethyl fluorocarbamate and 3.6 g (0.050 mol) of ethyl vinyl ether. An exothermic reaction began immediately, and external cooling was required to keep the reaction temperature below 45°. After 10 min, the mixture was distilled through a 25-cm Holzmann column to give 7.0 g (78% yield) of ethyl N-α-ethoxyethyl-N-fluorocarbamate bp 35–36° (0.2 mm).

Anal. Calcd for $C_7H_{14}NFO_3$: C, 46.92; H, 7.88; N, 7.81; F, 10.6. Found: C, 46.41; H, 7.80; N, 7.9; F, 10.8.

The proton nmr spectrum (CCl_4 solution) consisted of a doublet (J_{HF} = 33 cps) of quartets (J_{H-CH_3} = 6 cps) at δ 5.24 for the methine, a quartet (J = 7 cps) at 4.26 for $-CO_2CH_2CH_3$, a multiplet at 3.63 for $CH_2OCH_2CH_3$, and superimposed methyl signals at 1.35. The fluorine spectrum consisted of a doublet (J_{HF} = 33 cps) at ϕ^* +96.3. The infrared spectrum showed carbonyl peaks at 5.68 and 5.80 μ.

Ethyl N-Cyclohexyl-N-fluorocarbamate. Cyclohexene (3.3 g, 0.040 mol) was added dropwise, with stirring, to a solution of 4.3 g (0.040 mol) of ethyl fluorocarbamate in 22 ml of concentrated sulfuric acid at 0–5°. The reaction was then maintained at 24–25° for 45 min; occasional cooling was required. The mixture was poured onto 80 g of ice and the product was extracted with four 20-ml portions of methylene chloride, dried over Drierite, and distilled to give 6.2 g (82% yield) of ethyl N-cyclohexyl-N-fluorocarbamate, bp 50–51° (0.1 mm), $n^{25}D$ 1.4430.

Anal. Calcd for $C_9H_{16}NO_2F$: C, 57.12; H, 8.52; N, 7.40; F, 10.0. Found: C, 56.72; H, 8.65; N, 7.65; F, 10.5.

The infrared spectrum showed carbonyl bands at 5.70 and 5.83 μ. The proton nmr spectrum consisted of a triplet at δ 1.26 and a quartet at 4.16 for the ethoxy group, a broad multiplet at 1.71 for the methylenes, and a broad doublet (J_{HF} = 37.2 cps) at 3.75 for the methine. The fluorine spectrum consisted of a doublet (J = 39 cps) at ϕ^* +92.1.

Ethyl N-Cyclopentyl-N-fluorocarbamate. The reaction of 6.43 g (0.060 mol) of ethyl fluorocarbamate with 4.1 g (0.060 mol) of cyclopentene in 30 ml of sulfuric acid, using the above procedure, gave 3.5 g (34% yield) of ethyl N-cyclopentyl-N-fluorocarbamate, bp 39° (0.2 mm), $n^{25}D$ 1.4375.

Anal. Calcd for $C_9H_{14}NFO_2$: C, 54.84; H, 8.05; N, 8.00. Found: C, 54.40; H, 7.99; N, 8.21.

The proton nmr spectrum (CCl_4 solution) consisted of a triplet at δ 1.33 and a quartet at 4.25 for the ethoxy group, a multiplet with maximum intensity at 1.75 for the ring methylenes, and a quintet (J_{HH} = 8 cps) of doublets (J_{HF} ~ 40 cps) at 4.5 (partially obscured by the quartet) for the methine. The fluorine spectrum consisted of a doublet (J = 44 cps) at ϕ^* +89.7. The infrared spectrum showed carbonyl peaks at 5.67 and 5.80 μ.

Methyl N-Carbethoxy-N-fluoro-β-aminopropionate. Methyl acrylate (4.3 g, 0.050 mol) was added over a 15-min period, with stirring, to a solution of 5.4 g (0.050 mol) of ethyl fluorocarbamate in 20 ml of concentrated sulfuric acid at 5 to 10°. The solution was allowed to stand at ambient temperature for 90 min and was then poured onto 100 g of ice. The product was extracted with four 30-ml portions of methylene chloride, dried over Drierite, and distilled to give 1.3 g of ethyl fluorocarbamate and 5.1 g (50% yield, 70% conversion) of methyl N-carbethoxy-N-fluoro-β-aminopropionate, bp 52–54° (0.1–0.3 mm), $n^{25}D$ 1.4235.

Anal. Calcd for $C_7H_{12}NO_4F$: C, 43.52; H, 6.26; N, 7.25; F, 9.84. Found: C, 43.30; H, 6.17; N, 7.15; F, 10.2.

The infrared spectrum showed the following peaks (μ): 3.35 (m), 3.40 (m), 5.77 (s), 6.97 (s), 7.3 (s), 7.58 (s), 8.0 (s), 8.37 (s), 8.5 (s), 8.63 (m), 9.3 (m), 9.78 (m), 10.72 (w), 11.12 (w), 11.55 (w), and 11.85 (w).

The proton nmr spectrum consisted of a triplet at δ 1.35 and a quartet of 4.23 for the ethoxy group, a methoxy signal at 3.65, a doublet (J_{HF} = 34 cps) of triplets (J_{HH} = 8 cps) at 3.93 for $-NFCH_2CH_2CO_2CH_3$, and a triplet (J = 7 cps) at 2.65 for $CH_2CH_2CO_2CH_3$. Unreacted starting materials were recovered in a similar reaction that was quenched immediately after the addition was completed.

Diisopropyl Carbonate. A solution of 2.1 g (0.0151 mol) of isopropyl difluorocarbamate in 10 g of isopropyl alcohol was heated at 60° for 4 hr. Distillation gave 1.2 g (61% yield) of diisopropyl carbonate, bp 42–43° (12 mm), $n^{25}D$ 1.3870 (lit.[21] bp 42.5–43° (12 mm), $n^{20.6}D$ 1.3906).

Difluoramine. Isopropyl difluorocarbamate (4.2 g, 0.030 mol) was added dropwise, with stirring, to 30 ml of 25% sulfuric acid under a stream of nitrogen. Rapid gas evolution took place when the mixture was heated to 70°. The product, passed through a tube containing Drierite, and collected in a −80° trap, consisted of 1.05 ml (89% yield) of difluoramine containing 10% carbon dioxide. The product was identified by its infrared spectrum.[20]

Chlorodifluoramine. Butyl difluorocarbamate (0.30 g, 0.0020 mol) was added with a dropping funnel to 20 ml of 5.3% sodium hypochlorite at 5° in an evacuated 50-ml flask fitted with a manometer, a thermometer, and an infrared gas cell. No gas was liberated at this temperature, but warming the solution to 30° liberated 0.000714 mol of chlorodifluoramine (160 ml at 84 mm and 30°, 36% yield). The infrared spectrum was identical with that in the literature;[20] CO_2 and N_2F_4 were not detected.

Acknowledgment. The authors wish to thank Dr. H. M. Nelson and Mr. L. A. Maucieri for the nmr analysis and Mr. K. Inouye for the elemental analysis.

(21) K. W. F. Kohlrausch and R. Sabathy, *Monatsh.*, **72**, 308 (1939).